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## Abstract

Ideal marine antifouling/fouling release surface coatings should be non-leaching and non-toxic, while effectively resisting the attachment of marine organisms or easily releasing them post-attachment. This program aims to fundamentally understand the spatial and temporal chemistry and physics required for new polymer-based antifouling surfaces, based on dynamic structures which respond to their chemical environment. Our work focuses on preparing and testing polymers brush surfaces with amphiphilic structures. In this report, we summarize a pattern formation approach, based on surface-grown copolymer brushes with new chemical compositions, allows us to determine and test the effect of new chemical and topological pattern length scales on the adhesion of marine organisms.

In the past year, we have engineered a novel approach for complex surface functionalization with polymer brushes. This was spawned by previous research which showed significant alteration of surface properties upon immersion in water for our previous diblock copolymer patterning approach (see previous ONR report). Using this new approach, we combined and characterized different chemistries in close proximity to one another with high spatial resolution. These surfaces have been synthesized and characterized with multiple techniques, including surface analytical methods such as imaging X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), as well as surface tensiometry. These physical methods, help us understand the nature of the coating surface and how antifouling behavior develops.

## Technical Objectives

### Introduction

Marine biofouling on naval vessels is a persistent and highly undesirable problem. The increase in roughness imparted by the accumulation of biofouling leads to not only increased drag and substantial energy and security penalties, but also promotes bio-corrosion. The consequent increase in dry docking time and frequent maintenance results in a large financial burden for the marine industry, and has spawned increasing interest in antifouling/fouling release coatings to protect these engineered structures. Historically, biocide containing or releasing paints have been used to address this issue. However, these toxic biocides such as tin, copper, lead, arsenic, mercury and their organic derivatives (such as organotin) have been banned in many countries due to the environmental risks they posed. Unfortunately, the leached toxins accumulate in marine

environments, especially near ports and harbors, and are dangerous for non-target marine organisms and humans by partitioning of metabolic functions. In recent years, with increased legislation on toxicity requirements, the research community has been actively exploring and developing new, robust, and environmentally benign alternative coating materials that inhibit attachment and reduce adhesion strength to prevent biofouling.

In particular, polymer coatings incorporating amphiphilic structures have shown some remarkable characteristics and received considerable attention. It has been suggested that since they contain both hydrophobic and hydrophilic components, they can form “ambiguous surfaces”. They may offer a partial solution to universal antifouling/fouling release coatings, capable of both resisting settlement, as well as releasing a wide variety of fouling organisms. As an example, amphiphilic copolymers containing perfluorocarbon and poly(ethylene glycol) (PEG) side chains have been evaluated using settlement and release assays of *Navicula* diatoms and *Ulva Linza* spores. The results showed comparable or improved antifouling and release properties over traditional PDMS-based coatings. However, up until now there is little understanding of why these systems work, hindering attempts to rationally design coatings with further improved antifouling/fouling release properties.

The goal of our research therefore is to develop novel non-toxic, easily processable, environmentally benign antifouling and/or fouling-release marine coatings with improved performance compared to both currently utilized copper ablative and PDMS based coatings, proving effective against as wide a spectrum of fouling organisms as possible. We further aim at using our expertise in the characterization of the films we produce to improve a fundamental understanding of how and why certain materials work better than others.

## Research Approach

New surface coatings have been created using visible light-mediated living radical polymerization of methacrylate-based, anti-fouling relevant monomers. We have investigated polymerization kinetics for homo- and diblock copolymer brushes by means of optical thickness measurements and X-ray reflectivity on poly(trifluoroethyl methacrylate) (TFEMA) and poly(ethylene glycol methacrylate) (PEGMA) polymer brushes. Further, we patterned these two monomers to give topographically and chemically well-defined ambiguous surfaces which combine hydrophilic and hydrophobic properties on the micron length scale. X-ray photoelectron spectroscopy (XPS) and dynamic secondary ion mass spectroscopy (*d*SIMS) allowed us to precisely determine chemical surface composition while atom force microscopy (AFM) afforded precise analysis of topographical features inherent to patterning. In the past year in particular, our work has been focused on circumventing some problems with wettability, enhancing monomer scope and processability of our polymer brush-based coatings

## Progress Statement

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## 1 Patterned materials

### 1.1 Introduction

Despite extensive studies on a vast number of anti-biofouling systems, no clear consensus has emerged regarding which surfaces and assorted building blocks are best suited to prevent fouling. Visible light mediated polymerization can serve as a model platform to elucidate the properties of sophisticated and complex ambiguous anti-fouling films. This approach enables investigations into the precise structure/property relationships for a broad range of anti-fouling relevant chemical species by combining multiple anti-fouling approaches simultaneously: hydrophilicity, hydrophobicity, and well-defined spatial ambiguity. Our strategy readily allows precise adjustment of chemical surface composition through the simple use of photomasks for visible light-mediated, spatially well-defined chain extension of homopolymer brushes to AB-diblock copolymer brushes.

The mechanism of polymerization follows visible absorption of a *fac*-Ir[(ppy)<sub>3</sub>]<sup>1</sup> photocatalyst whose excited species, Ir<sup>III\*</sup> reduces an alkyl bromide initiator to give an alkyl radical for polymerization of the monomer. The highly oxidizing Ir<sup>IV</sup> complex can subsequently react with the propagating radical to reform the initial Ir<sup>III</sup> ground state complex and a dormant polymer chain with a brominated end functionality. The presence of active radical species only at locations where light interacts with the catalyst affords spatially confined polymerization with fidelity theoretically limited only by radical diffusion lengths

This photochemically controlled, living atom-transfer radical polymerization-based process poses many advantages for application in polymer brushes for anti-fouling by covalently binding initiators onto various substrates and pursuing a grafting-from approach. In addition to the above mentioned advantages of high grafting densities and film thicknesses, the living character affords facile synthesis of a series of interesting topographically and chemically patterned surfaces.

### 1.2 Previous Work and Motivation

Dense and thick diblock copolymer brushes were prepared under visible light-mediated living radical polymerization conditions<sup>[1,2]</sup> and a  $\lambda = 405$  nm collimated LED light source. The mechanism of polymerization follows visible light absorption of a *fac*-Ir[(ppy)<sub>3</sub>] photocatalyst whose excited species, Ir<sup>III\*</sup>, transfers an electron to the initiating  $\alpha$ -bromo ester to form a reactive alkyl radical. The highly oxidizing Ir<sup>IV</sup> complex can subsequently react with the propagating radical to reform the initial Ir<sup>III</sup> ground state complex and a dormant bromo chain end functionality.<sup>[1,2]</sup> In contrast to traditional surface-initiated polymerizations, the use of a photocatalyst readily affords well-defined topographically and chemically patterned surfaces and/or spatially confined post-

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<sup>1</sup>ppy = 2-pyridylphenyl.

functionalization by simply employing photomasks. Furthermore, this Ir-mediated polymerization is readily turned on and off by light without loss of the bromide chain end. Therefore, surface grafted  $\text{A-}b\text{-B}$ -diblock<sup>2</sup> or even multi-block copolymer brushes can be prepared. Finally, the use of light in the visible wavelength region prevents undesired side-reactions that are possible with UV-based lithography techniques (e.g. UV thiol-ene click chemistry post-functionalization).<sup>[3]</sup>

High grafting densities and film thicknesses, inherent to such SI-CRPs, render this method an ideal candidate for the formation of both homogeneous and patterned surfaces for anti-fouling applications.<sup>[4]</sup> Studies suggest that the spatially ambiguous combination of hydrophilic and hydrophobic polymers creates surfaces which inherently prevent the foulant from attaching. We therefore studied the polymerization kinetics for different classes of anti-fouling relevant monomers, both hydrophilic and hydrophobic. The former includes both PEG-based macromonomers such as poly(ethylene glycol methacrylate) (PEGMA).

Employing this technique yielded diblock copolymer brushes of PEGMA and TFEMA. In a series of experiments, the initial thickness of the A-homopolymer brush layer was varied while the polymerization time for the top B-block was held constant at 15 min. A resulting library of  $\text{p(PEGMA}_n\text{-}b\text{-TFEMA}_{15})$ , and  $\text{p(TFEMA}_n\text{-}b\text{-PEGMA}_{15})$ , ( $n = 15, 30, 45$ , and  $60 \text{ min}^3$ ) diblock brushes of different compositions allowed us to systematically study how the ratio of these monomers influences the chemical surface composition of these  $\text{A-}b\text{-B}$  diblock brushes.

In our last report we described the use of X-ray photoelectron spectroscopy (XPS) to quantify the chemical composition of the top ~10 nm of TFEMA/PEGMA diblock copolymer brush films. XPS confirmed the presence of  $\text{CF}_3$  at the surface and quantification showed that PEG C–O remains at the surface for all  $\text{p(PEGMA}_n\text{-}b\text{-TFEMA}_{15})$  diblock brushes. However, as described in our report the extension of  $\text{p(TFEMA)}$  homopolymer brushes with PEGMA, is more challenging. Experimentally, the hydrophobicity of the initial  $\text{p(TFEMA)}$  brush renders wetting with the hydrophilic PEGMA monomer difficult. Polymer chain extension is consequently not as pronounced and film thicknesses do not increase as much as for the  $\text{p(PEGMA}_m\text{-}b\text{-TFEMA}_{15})$  diblocks. This is especially the case for thicker initial  $\text{p(TFEMA)}$  films. Copolymerization difficulties are also thought to be related to the collapse of brush conformations, i.e., the burying of the reactive bromo chain ends due to the high surface activity of the fluorinated repeat units, which imposes additional steric hindrance for backbone extension.

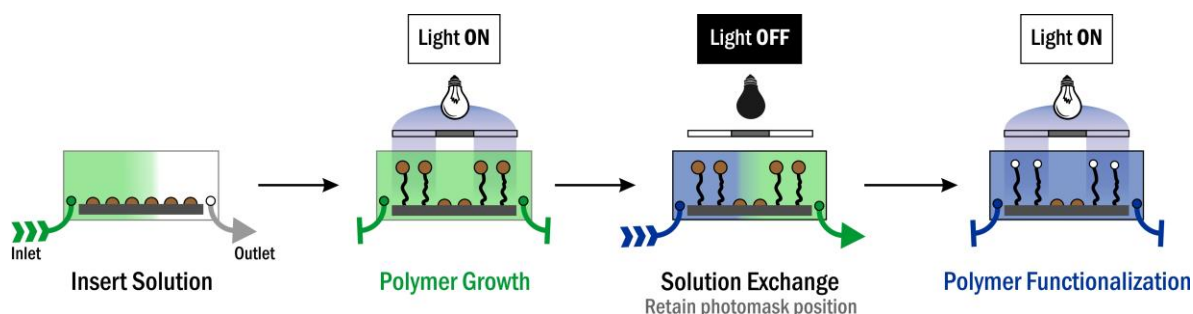
### 1.3 Concept and Idea

In an attempt to solve this problem and produce binary functionalized substrates without the above diblock strategy, we combined stopped-flow techniques<sup>[7]</sup> and reduction photolithography<sup>[8]</sup> to engineer a modular platform for sequential photochemical reactions in a continuous manner. This facilitates chemical surface patterning through successive exchange of reactants within a stop-flow cell, while providing significant flexibility to exchange light sources, and/or spatially decoupled photomasks. **Scheme 1** illustrates such a photochemical sequence: Spatially controlled photopolymerization, followed by exchange of the solution within the stop-flow cell, and then secondary functionalization of polymer brushes, in this case by light-mediated removal of the active terminal bromine chain end. During this entire process, neither wafer nor photomask are moved, which allows spatial confinement of functionalization exclusively to regions where polymer brushes were previously grown. As a direct consequence, adjacent surface-grafted polymerization

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<sup>3</sup> Subscripts  $n$  and  $m$  denote the polymerization time for the respective block in minutes.

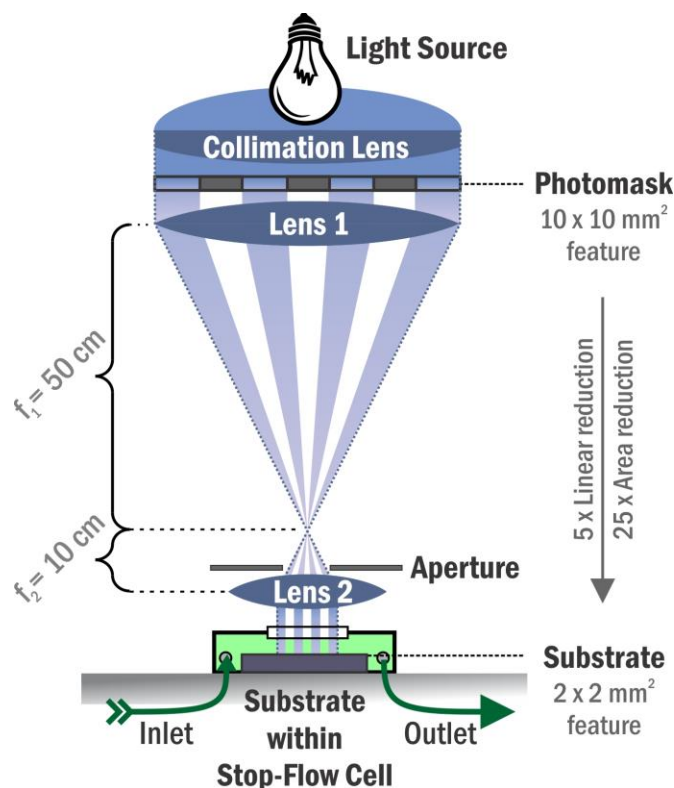
initiators remain untouched, affording hierarchical chemical patterning on uniformly functionalized substrates. This renders repetitive initiator deposition and related cleaning/treatment steps unnecessary and results in economic and environmental advantages. Ultimately, this *Solution Exchange Lithography* concept streamlines the production of chemically patterned surfaces and affords access to hierarchically structured substrates, all from uniform initiating layers.



**Scheme 1.** Concept of Solution Exchange Lithography. Enclosing a substrate in a stop-flow cell allows for in-situ exchange of reactants and execution of successive chemical reactions at precisely the same location. Illustrated here is light-mediated growth of polymer brushes followed by solution exchange and subsequent, spatially-controlled passivation of the active polymer chain ends.

## 1.4 Experimental Setup

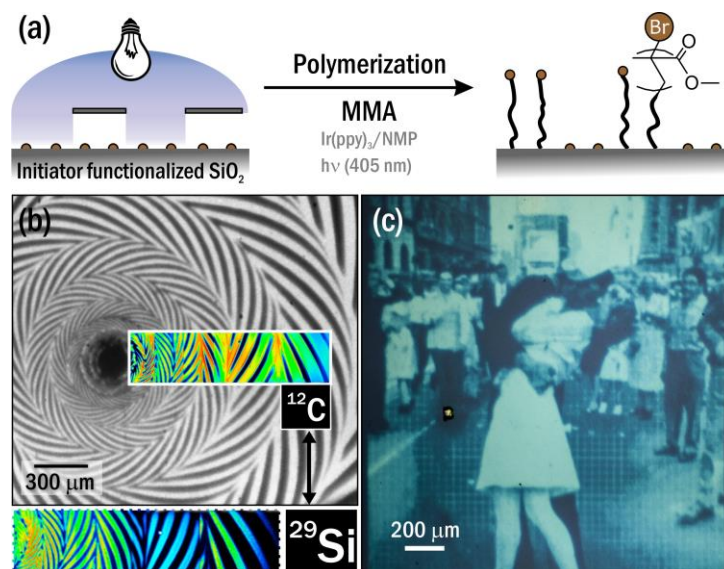
The experimental setup involves an array of lenses to optically reduce and project an inkjet-printed photomask onto a substrate positioned inside a stop-flow cell (see **Figure 1**). This stop-flow cell was readily scaled to accommodate large wafers of  $\varnothing = 3''$  diameter, enhancing both the relevance and potential of this process, with the immediate proximity between cover glass and substrate allowing capillary forces to uniformly spread the reactants over the surface. Reduction projection reproduces the image from an original photomask on a surface with reduced size. This concept facilitates alignment and/or stacking of multiple patterns by eye, paving a path towards complex microscopic patterns from macroscopic photomasks. The ratio of the focal lengths of the two lenses ( $f_1$  and  $f_2$ ) determines the linear reduction factor,  $LRF = f_1/f_2$ , which could readily be adjusted by simply exchanging lenses. For this work, focal lengths of  $f_1 = 500$  mm and  $f_2 = 100$  mm were used, resulting in optical reduction by a factor of five (area reduction to  $1/25^{\text{th}}$ ). This spatial decoupling (separating) of the photomask(s) from the substrate has a number of benefits. The non-contact-based nature allows use of inexpensively produced, inkjet-printed photomasks. If desired, simple x,y-translation of the substrate stage allows lateral repetition of either a single or multiple patterns. In addition, all processing steps, including chemical reactions, rinsing, and drying can be performed without removing the substrate from its original position. This allows successive, spatially well-defined (photo)chemical reactions to be performed sequentially from uniform initiating layers, including both traditional<sup>[9]</sup> and light-mediated controlled radical polymerization,<sup>[1,2,4,10–14]</sup> dehalogenation,<sup>[15]</sup> thiol-ene coupling,<sup>[16,17]</sup> and atom transfer radical addition,<sup>[5,18]</sup> As an added benefit, the stop-flow cell is sealed from the surrounding environment and is readily filled via cannula transfer. This enables oxygen-sensitive reactions to be performed under simple conditions, without the need for a glove box or other Schlenk-technique related equipment.



**Figure 1.** Schematic of Solution Exchange Lithography. An array of lenses is used to project the pattern of a photomask onto a substrate which is enclosed in a stop-flow cell. At focal lengths of  $f_1 = 500 \text{ mm}$  and  $f_2 = 100 \text{ mm}$ , this projector reduces features of the photomask image by a linear reduction factor of  $\text{LRF} = 5$  (25x reduction in area) and reproduces them on the surface. Spatially decoupling the stop-flow cell from the photomask allows exchange of solutions while retaining the exact position of the photomask, enabling sequential stop-flow photochemistry.

### 1.5 Proof of concept and homopolymer patterning

**Figure 2** demonstrates the potential of this setup for the controlled radical photopolymerization<sup>[1,4,19]</sup> growth of patterned poly(methyl methacrylate) poly(MMA) brushes with high spatial fidelity. The resulting topographical patterning was revealed by optical microscopy and Secondary Ion Mass Spectrometry (SIMS), where carbon ( $m/z = 12$ , poly(MMA)) fragment maps indicated successful reproduction of the original photomask image (see Figure 2). Correspondingly, silicon ( $m/z = 29$ ) was detected exclusively in regions of the  $\text{SiO}_2$  substrate where the photomask blocked the light and no polymer was grown, with the smallest obtainable line features being a function of both initial feature sizes and optical reduction. At  $\text{LRF} = 5$ , the total area of the resulting reduced pattern ( $2 \times 2 \text{ mm}^2$ ) was 4% of the original inkjet-printed photomask ( $10 \times 10 \text{ mm}^2$ ). For the experiments described herein, features as small as  $2 \mu\text{m}$  were obtained. As previously reported, simple variation of either polymerization time and/or photon flux may be used to target different brush heights, and a majority of polymer chain ends remain active for additional functionalization or further growth.<sup>[4,13,19]</sup> This approach was shown to be compatible with both conventional photomasks as well as with inkjet-printed overhead transparencies, affording the reproduction of arbitrarily complex patterns and manufacturing of surfaces combining numerous polymer brush height gradients on a single substrate.



**Figure 2.** (a) Schematic of light-mediated controlled radical polymerization of methyl methacrylate (MMA) by irradiation of an initiator-functionalized SiO<sub>2</sub> substrate through a binary photomask. Brown circles indicate polymerization initiators. (b and c) Optical micrographs of different poly(MMA) (light) polymer brush patterns on SiO<sub>2</sub> (dark) illustrate the achievable spatial resolution. Insets in (b) represent maps for carbon ( $m/z = 12$ ) and silicon ( $m/z = 29$ ) fragments obtained via Secondary Ion Mass Spectrometry.

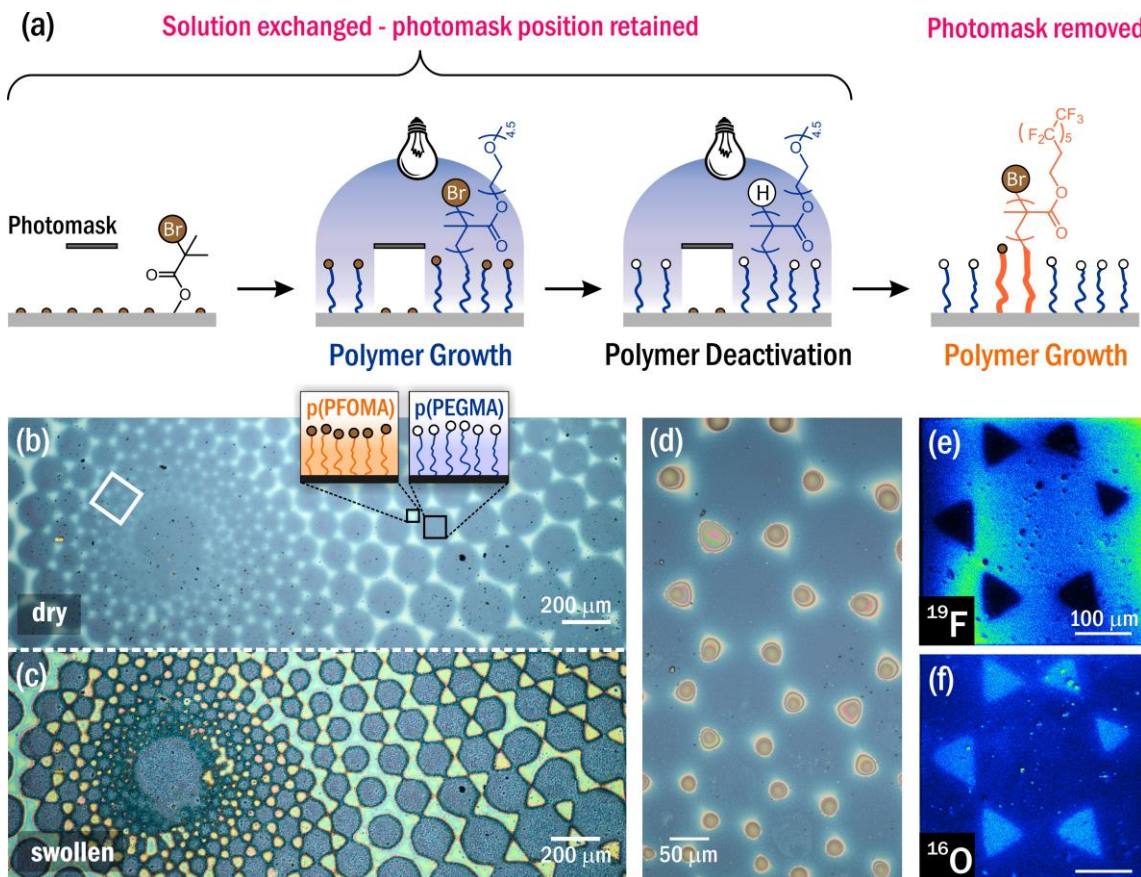
## 1.6 Fabrication of hydrophilic/hydrophobic binary brushes

The ability to exchange reactants in-situ while retaining the position of the photomask is a significant advantage when chemically patterning polymer brushes. The use of sequential photochemical reactions allows preparation of chemically versatile surfaces, as demonstrated by preparation of binary polymer brush patterns. Such binary patterned substrates offer lateral combination of different functional materials with contrasting physical properties and represent an intriguing pathway towards surfaces which selectively adapt to their environment.<sup>[20]</sup> However, in conventional processes, the preparation of binary polymer brushes with micron-scale feature sizes requires tedious and iterative deposition of initiator patterns, subsequent pattern amplification (via SI-CRP), followed by chain end passivation (vide supra).<sup>[21]</sup> To the best of our knowledge, no established method has been capable of fabricating binary patterned brushes from uniform initiator layers.

In contrast, the setup described herein allows for the preparation of binary brushes from a *uniform initiating layer* via *sequential stop-flow photochemistry*. Eliminating the repetitive initiator deposition steps not only facilitates processing, but also prevents related chemical contamination. **Figure 3a** illustrates the formation of such a chemically patterned, binary surface with disparate wetting properties. Initially, patterned poly(ethylene glycol) methacrylate (PEGMA) brushes were grown by irradiation through a photomask. Then, without moving the photomask, reactants within the stop-flow cell were exchanged and a solution of a highly reducing photocatalyst was inserted to promote spatially controlled dehalogenation of the polymer brush chain end.<sup>[15]</sup> Because the photomask remains in its original position, this subsequent, light-mediated passivation reaction is locally confined to where the initial PEGMA polymerization occurred. The poly(PEGMA) brushes are therefore selectively deactivated and cannot participate in subsequent polymerizations. Surface-bound polymerization initiators that did not participate in the initial polymerization remain active and allow a third sequential reaction to be performed, i.e., growth of 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (PFOMA) polymer brushes via atom transfer radical polymerization (ATRP). Optical



microscopy (Figure 3b-d) and SIMS (Figure 3e, f) confirmed the topographical and binary chemical nature of the resulting substrate with fluorine ( $m/z = 19$ , poly(PFOMA)) and oxygen ( $m/z = 16$ , poly(PEGMA)) fragment maps matching the positive and negative representation of the original photomask, respectively. These binary patterns were also accessible by substituting the dehalogenation step (cf. Figure 3a) with spatially controlled chain end passivation via atom transfer radical addition,<sup>[5,18]</sup> highlighting the compatibility of this platform with a range of light-mediated reactions.



**Figure 3.** (a) Formation of binary brushes via a cascade of sequential photochemical reactions. Photopolymerization of poly(ethylene glycol) methacrylate (PEGMA) is followed by light-mediated dehalogenation (local deactivation of polymer brush chain ends). The photomask remains in place while reactant solutions are exchanged. Lastly, the photomask is removed and 1H,1H,2H,2H-perfluorooctyl methacrylate (PFOMA) is polymerized via atom transfer radical polymerization. (b) Optical bright-field micrograph of dry binary polymer brushes. (c) Lateral combination of hydrophilic and hydrophobic properties allows for selective swelling in a high humidity environment. (d) Water droplets are formed exclusively in hydrophilic regions. Secondary Ion Mass Spectrometry indicates spatial confinement of fluorine (e) and oxygen (f) fragments, providing additional evidence for the chemically binary nature of the surface.  $^{16}\text{O}$  and  $^{19}\text{F}$  maps obtained from the white rectangular region in (b) represent the positive and negative of the original photomask, respectively.

The preparation of binary hydrophilic poly(PEGMA) and hydrophobic poly(PFOMA) brushes from incompatible monomers further serves to demonstrate the breadth of accessible materials. Their significantly contrasting wetting properties are evident from their water contact angles,  $\theta_{\text{PEGMA}} = 61^\circ$  and  $\theta_{\text{PFOMA}} = 120^\circ$ , which, according to the Young-Dupré equation, correspond to

surface energies of  $W_{\text{PEGMA}} = 0.11 \text{ J m}^{-2}$  and  $W_{\text{PFOMA}} = 0.04 \text{ J m}^{-2}$ , respectively.<sup>[22]</sup> Spatially confined, hydrophilic poly(PEGMA) regions are observed to selectively swell upon increasing humidity (see Figure 3c), increasing the poly(PEGMA) brush height and promoting localized water droplet formation, i.e., selective wetting (Figure 3d). The synthesis of such continuous binary patterns from uniform initiating layers offers significant opportunities and directly relies on the ability to *exchange reactants in-situ*, allowing for sequential photochemical procedures while *retaining the position of the photomask*.

## 1.7 Conclusion

In conclusion, this report outlines the design and application of Solution Exchange Lithography for patterning of anti-fouling relevant polymers. It illustrates the versatility and modular nature of this novel platform for surface patterning. This approach circumvents the need for repetitive initiator deposition, as is common in many conventional techniques, and allows preparation of patterned surfaces with large topographical and chemical variety from uniform initiating monolayers. Key to these advances is the ability to exchange reaction solutions in-situ, leading to homogeneous wetting of substrates with solutions of vastly contrasting polarity. Eliminating the necessity to remove the substrate between individual processing steps enables successive reactions to be performed in the same location with micron-scale resolution. In addition, all procedures, including oxygen-sensitive reactions, can now be performed in a closed stop-flow cell and without the necessity of a glovebox, while the decoupling of photomask and wafer allows the use of inexpensive, inkjet-printed overhead transparencies as photomasks, significantly reducing both time and cost related to fabrication of standard photomasks.

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## Refereed Journal Articles

C. W. Pester, J. E. Poelma, B. Narupai, S. N. Patel, G. M. Su, T. E. Mates, Y. Luo, C. K. Ober, C. J. Hawker, and E. J. Kramer. Ambiguous anti-fouling surfaces: facile synthesis by light-mediated radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 54, 253..

C. W. Pester, B. Narupai, K. M. Mattson, D. P. Bothman, D. Klinger, K. W. Lee, E. H. Discekici, and C. J. Hawker. Engineering Surfaces through Sequential Stop-Flow Photopatterning. **2016**, *submitted*.

## Books and Chapters

None

## Technical Reports

None

## Contributed Presentations (Christian Pester, Craig Hawker):

C. W. Pester, B. Narupai, K. M. Mattson, D. P. Bothman, K. W. Lee, E. H. Discekici, D. Klinger, and C. J. Hawker. Solution Exchange Lithography. *Oral Presentation*, MRS Spring Meeting 2016 (Phoenix, AZ, USA)

C. W. Pester, B. Narupai, K. M. Mattson, D. P. Bothman, K. W. Lee, E. H. Discekici, D. Klinger, and C. J. Hawker. Solution Exchange Lithography. *Poster Presentation*, Materials Research Outreach Program Symposium 2016 (Santa Barbrara, CA, USA)

C. W. Pester, B. Narupai, K. M. Mattson, D. P. Bothman, K. W. Lee, E. H. Discekici, D. Klinger, and C. J. Hawker. Solution Exchange Lithography. *Poster Presentation*, Edward J. Kramer Memorial Symposium 2016 (Santa Barbrara, CA, USA)

C. W. Pester, J. E. Poelma, C. J. Hawker, and E. J. Kramer. Ambiguous copolymer surfaces from light-mediated radical polymerization. *Oral presentation*, DPG Spring Meeting **2015** (Berlin, Germany).

## Honors

2015      Craig Hawker, Dow Lecturer, Northwestern University

2015      Craig Hawker, Sproull Lecturer, Cornell University

2015      Craig Hawker, Purves Lecturer, McGill University

2015      Craig Hawker, The Grandpierre Lecturer, Columbia University

2015      Craig Hawker, Eli Lilly Distinguished Lecturer, Colorado State University

2015      Craig Hawker, Pettitt Lecturer, University of Texas, Austin

## **Related Sponsored Work**

**Project/Proposal Title:** Materials Research Science & Engineering Center at UCSB

(PI: Craig Hawker, Co-PI: Ram Seshadri, with 25 Senior Investigators)

**Source of Support:** National Science Foundation (DMR 1121053)

**Total Award Period Covered:** 9/2011-8/2017

**Project/Proposal Title** New Synthetic Methods for Advanced Polymeric Materials

(PI: with Kramer & Fredrickson)

**Source of Support:** The Dow Chemical Company

**Total Award Period Covered:** 11/2013-10/2015

**Project/Proposal Title:** Development of Sequence Controlled Polymers for Antibacterial  
Therapeutics and Coatings

(PI: W. Gutekunst)

**Source of Support:** NIH Fellowship

**Total Award Period Covered:** 9/2013-9/2016